

Chapter 4

EXPERIMENTAL TECHNIQUES AND RESULTS IN FLASH PYROLYSIS

4.1 EXPERIMENTAL TECHNIQUES

As set out in the general introduction, the survey of experimental results will be confined to flash pyrolysis at the exclusion of slow pyrolysis or carbonization. Flash pyrolysis poses three experimental difficulties that need careful consideration: (i) control and measurement of the temperature-time history of the coal particles (ii) suppression of secondary reactions (iii) quantitative collection of products.

The temperature-time history of the coal particles generally consists of a heating period, a period at approximately constant temperature and a cooling or quenching period. While isothermal operation permits the easiest kinetic analysis of the results, the reaction occurring during the heating and cooling times is often significant. The kinetic analysis of the data in this case must take into account the full temperature-time history. Whether or not the pyrolysis occurs isothermally, the measurement of the coal particles' temperature is not trivial. In many cases the temperature cannot be directly measured but must be calculated from a heat transfer model. The other two experimental problems, the suppression of secondary reactions and the collection of products, depend on the reactor geometry and flow pattern and are best discussed separately for the entrained flow and the captive sample techniques.

4.1.1. The entrained flow technique

In this experimental set-up shown schematically in Fig. 4.1, coal particles 20-100 μm are carried by a primary stream of an inert gas through a water-cooled injector at the axis of a vertical furnace. A secondary and larger stream of inert carrier gas flows downward along the furnace under laminar flow to assure that the particles are not dispersed radially to the furnace walls. Particles and volatile products are collected by a water-cooled probe of special design ensuring representative samples. The reaction time is adjusted by the flowrate of the secondary stream and the axial location of the probe. Heating elements around the furnace produce a uniform wall temperature in the middle zone of the furnace. The secondary gas stream is pre-heated to decrease the heating time.

A system of this type has been used by several workers (refs. 55-59). Kobayashi et al. (ref. 57) discuss in detail the experimental aspects of the technique and provide an analysis of the heating history of the particles including the effect of injector geometry and the mixing between primary and secondary gas streams. Their calculations indicate heating times in the range 5-50 ms. The times required for 40% weight loss of a bituminous coal varied in the range 10-100 ms as the

furnace temperature ranged from 2,100 to 1,500°K. Since the pyrolysis could not be assumed to occur at constant temperature, the kinetic analysis of the data incorporated suitable heat transfer calculations.

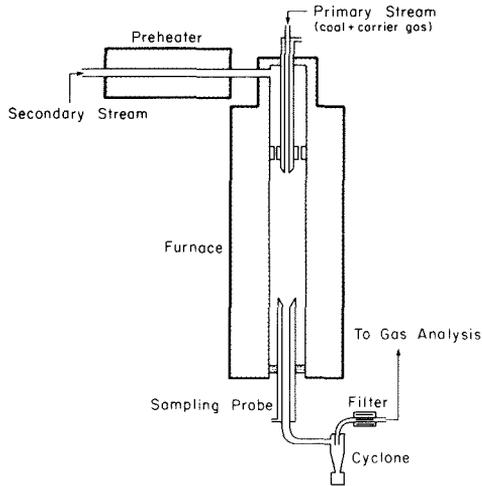


Fig. 4.1. Schematic of an entrained flow pyrolysis furnace. (source: ref. 59).

A second area of concern in the entrained flow technique is the secondary reactions suffered by the volatile reaction products during their residence in the furnace. These reactions make the mechanistic interpretation of product distribution somewhat doubtful but are of no great concern in combustion studies where the primary information required is weight loss and perhaps elemental composition of the volatiles.

The third experimental aspect of the entrained flow technique that requires careful consideration is the collection and analysis of products. In the aforementioned investigation (ref. 57) the weight loss was determined both directly and indirectly. The direct technique consisted of simply weighing the char collected in the probe. It was independently shown by cold flow experiments that the collection efficiency of char particles was 95 to 98%, suggesting similar accuracy in the measurements of the weight loss. The indirect technique employed the coal ash as a tracer. The results from this technique are independent of collection efficiency but are subject to some error due to vaporization of mineral matter

components.

In addition to the weight loss, certain of the gases (CO , CO_2 , SO_2 , NO_x) were determined by on-line continuous analyzers (ref. 59) or by gas chromatography (ref. 57). In some studies the solid char was characterized by Fourier-transform infrared spectroscopy (ref. 59). However, products of molecular weight above 200, usually classified as tar, could not be collected quantitatively. Condensation on the probe, the filter, the char, the walls of the gas collection vessel or the walls of the furnace itself preclude a quantitative analysis.

The furnace, injector, probe etc. described in references 57 and 59 represent the most careful and up-to-date designs. Earlier investigations using the entrained flow technique include that of Badzioch and Hawksley (ref. 56) who also used laminar flow conditions and that of Eddinger et al. (ref. 55) who used both laminar and turbulent flow conditions. The last study employed a large coal-to-gas mass flow ratio to provide sizeable tar samples. The increased amount of solids, however, interfered with the temperature measurements and increased the extent of secondary reactions.

4.1.2 The captive sample technique

A good description of this technique can be found in Anthony et al. (ref. 60). A small sample (5-200 mg) of ground coal is placed between the folds of a wire-cloth screen (see Fig. 4.2a) heated by a DC or AC current $I(t)$. The resistive assembly is attached inside a metal shell containing an inert gas or hydrogen. The gas pressure can be varied from vacuum to 100 at. In addition to providing the inert atmosphere at the desired pressure, the metal shell serves as a product collection vessel.

The coal sample is placed at the center of the screen where the temperature profile is relatively uniform. Near the electrodes the temperature drops due to conductive losses. A fast response (low mass) thermocouple serves to measure the temperature-time history. The sample size is chosen as a compromise of two considerations. A large sample minimizes the effect of coal inhomogeneity and generates a sufficient quantity of products for analysis. At the same time, however, a large sample of particles creates some irreproducibility because of possible rearrangement of the particles on the screen during heating. Samples of about 200-500 mg have been used by Solomon and Colket (ref. 61) and Gavalas and Wilks (ref. 62) allowing heating rates as high as 500°C/s and final temperatures as high as 1200°C . In the experiments of Anthony et al. (ref. 60) the sample size was 5-10 mg producing heating rates up to $10,000^\circ\text{C/s}$ with final temperatures as high as 1200°C .

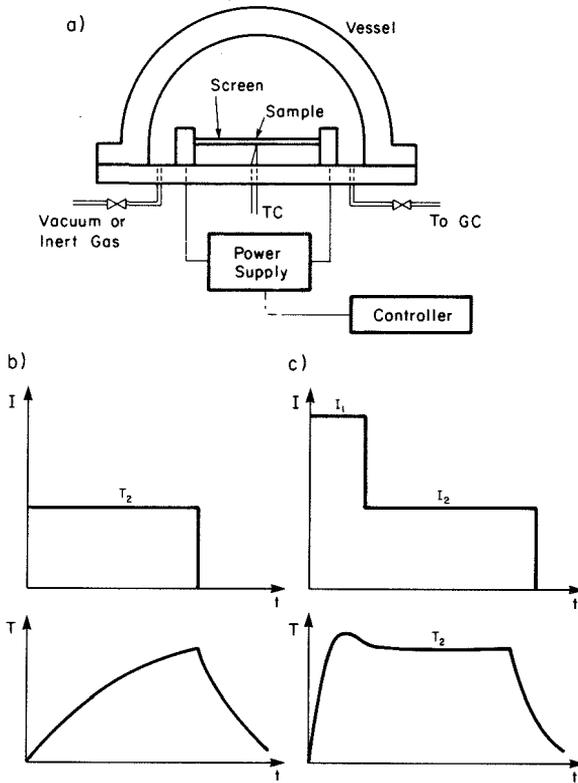


Fig. 4.2. The captive sample technique: (a) pyrolysis apparatus (b) single-pulse T - t response (c) double-pulse T - t response.

The temperature-time history $T(t)$ experienced by the coal sample depends on the current input $I(t)$, the geometry of the resistive assembly and surrounding shell and the nature and pressure of the surrounding gas. For given sample size and gas pressure, and for constant current I , the sample temperature reaches a steady state $T_s = f(I)$ at which the resistive heat input balances losses by conduction, convection and radiation (Fig. 4.2b). The time required to reach the steady temperature is usually on the order of seconds; therefore, constant current inputs are not suitable for producing large heating rates. To circumvent this problem, Anthony et al. (ref.60) applied current inputs consisting of two

consecutive pulses of constant current. If I_2 is the current required to produce the steady temperature T_2 , then switching from I_1 to I_2 approximately when the temperature has reached T_2 , produces the response shown schematically in Fig. 4.2c. The heating rate is thus limited only by the maximum current I_1 of the power supply.

Upon switching from I_1 to I_2 , the temperature overshoots slightly before settling to a constant level T_2 (Fig. 4.2c). The overshoot can be minimized by a proper choice of the current I_1 and the switching time. After being held at T_2 for the desired time, the sample is cooled by turning the current off. While the cooling period may last for a couple of seconds, after the first 200 ms or so the temperature becomes too low for the pyrolysis reactions to continue.

The most important items in product analysis are weight loss (total volatiles) and tar yield. The weight loss is determined by weighing the coal sample before and after pyrolysis. The tar condenses on aluminum foils lining the walls of the vessel. These foils can be removed and weighed after the completion of an experiment. The tar can be subsequently dissolved in a suitable solvent, e.g. tetrahydrofuran, for elemental analysis or nmr spectroscopy. Because of the short duration of each experiment the pyrolysis vessel remains cold ($T < 50^\circ\text{C}$ in most cases) and the recovery of tar on the aluminum foils is quite high. A small amount of tar remaining in the gas volume as vapors or aerosol can be collected by flowing the vessel contents through a filter (refs.63,64).

The gaseous products can be analyzed directly from the vessel or after collecting in suitable cold traps. Direct collection was used with sample sizes of 100-200 mg producing measurable concentrations of gases in the vessel (refs.61,62,65). Some experiments (ref.65) indicated that a nonnegligible fraction of the hydrocarbon gases were retained in solution in the tar deposited on the aluminum foil or on various surfaces in the vessel. To recover the gases quantitatively, it was found necessary after each pyrolysis run to heat the vessel to about $150\text{-}200^\circ\text{C}$ and thus drive the hydrocarbon gases to the gas phase. The heating in this case was accomplished by a mobile oven sliding on rails (ref.65). A disadvantage of this technique is that at $150\text{-}200^\circ\text{C}$ a certain fraction of light products in the tar would also enter the gaseous phase but would not be detected by the gas chromatographic procedure employed. The indirect technique of gas collection was developed by Suuberg (refs. 63,64) to concentrate the products derived from small sample sizes (about 10 mg). The contents of the vessel were flown through two cold traps packed with Porapak Q. The first trap maintained at room temperature retained intermediate products such as benzene, toluene and xylene. The second, maintained at -196°C by liquid nitrogen retained all gases except H_2 . The products were recovered by warming the traps at 240 and 100°C respectively.

In both the direct and the indirect technique the gaseous products were analyzed by gas chromatography employing a thermal conductivity detector for CO , CO_2 ,

H₂, H₂O and a flame ionization detector for hydrocarbons. The determination of water caused persistent difficulties. One difficulty was the uncontrolled adsorption-desorption of water from pyrolysis or from the atmosphere on vessel walls and gas lines. The other difficulty involved the integration of the broad and distorted chromatographic peak. Solomon and Colket (ref. 61) used a different and somewhat more reliable procedure for water determination.

The overall efficiency of product collection has varied among the various experimental setups employed. The best results seem to have been obtained by Suuberg, who reported (refs. 63,64) a 95% total mass balance and 90% balance on carbon and hydrogen. The largest analysis error is in water, as much as 40%, the lowest in hydrocarbon gases, 5-10%.

An interesting version of the captive sample technique has been described by Jüntgen and van Heek (ref. 66). The main features of the experimental setup was direct connection of the pyrolysis vessel with a time-of-flight mass spectrometer permitting direct on-line analysis of gaseous pyrolysis products and a facility for movie-camera recording of physical changes of the coal particles. A controlled power supply provided a linear temperature-time profile with heating rates up to 3,000°C/s.

4.1.3 The "pyroprobe"

In a variation of the captive sample technique, the coal sample is placed in a heated probe, the "pyroprobe", directly connected to the injection port of a gas chromatograph. The commercially available pyroprobe consists of a platinum ribbon as the heating element with associated power supply and control circuitry. Using coal samples of less than 5 mg, the heating element can supply heating rates up to 20,000°C/s and final temperatures up to 2,000°C. A helium or other inert carrier sweeps the pyrolysis products through a short line into the chromatographic column.

Among the reaction products, gases and compounds of intermediate volatility can be analyzed by using suitable separation columns. For example, capillary columns permit the elution of compounds as heavy as naphthalene and phenol. Heavy tars condense on tube walls or column packing and cannot be analyzed. The char residue is weighed at the conclusion of each experiment. Applications of the pyroprobe have been reported in refs. 67 and 68.

To conclude this section we summarize the relative merits of the three techniques described. The entrained flow technique is suitable for high temperature and short residence time pyrolysis where it provides the best temperature control and rapid quenching. The steady state operation allows the processing of a large quantity of coal to smooth sample inhomogeneity. Although gas and char collection is straightforward, tar collection is difficult. The captive sample technique involves much simpler apparatus and allows arbitrary pressure (including vacuum) and

residence time. Except at the highest temperatures, it allows good control of temperature and heating rates. However, high heating rates can be achieved only with small samples (~ 10 mg) exacerbating the problem of sample inhomogeneity. Product collection is good, although the milligram quantity tar collected in the case of small coal samples is insufficient for chemical characterization. Compared to the standard version of the captive sample technique, the pyroprobe arrangement is limited by small sample size and operation at close to atmospheric pressure. In addition, the pyroprobe does not allow the collection of heavy products. However, the direct injection of products into the chromatographic column is a very convenient feature and greatly reduces the turnaround time for an experiment. A more detailed discussion of the operating characteristics of various experimental arrangements is given in a recent comprehensive report by Howard et al. (ref. 69).

4.2 EXPERIMENTAL RESULTS AND DISCUSSION

This section contains a survey of data on weight loss, product distribution and product composition as functions of temperature and pyrolysis time. The bulk of the data reported here derive from essentially isothermal experiments, small particle size and low pressure (vacuum to 1 at). Limited results involving variations in the heating rate and temperature-time history will be discussed in conjunction with the kinetic modeling in chapter 6. Pressure and particle size are variables which affect the rate of transport processes, therefore they will be discussed in chapter 5 on heat and mass transfer. The results discussed in the present chapter relate to conditions which minimize interferences by transport phenomena and the concomitant secondary reactions. Our survey of experimental data is selective rather than extensive, emphasizing recent comprehensive work and altogether omitting earlier or more narrowly focussed studies. For a broader experimental survey the report of Howard et al. (ref. 69) is highly recommended.

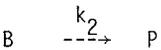
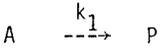
4.2.1 Weight loss

Although only an overall measure of the reaction's progress, the weight loss or total yield of volatiles displays a complex temperature dependence. To facilitate the discussion we introduce a few terms:

cumulative yield:	fraction or percentage of the <i>weight</i> of a product evolved during the period of pyrolysis relative to the weight of coal on an "as received" or dry ash-free basis; the cumulative yield is generally a function of temperature and time.
instantaneous yield:	the derivative with respect to time of the cumulative yield.

- yield: the term yield will be used as a short-cut for cumulative yield.
- ultimate yield: *at fixed temperature* the cumulative yield asymptotically reaches a maximum value, *within experimentally reasonable times*; this maximum value will be called the ultimate yield and is generally a function of temperature.

The ultimate yield defined above has relative rather than absolute significance. Consider for example two first order parallel and independent reactions with the same product,



If A_0 , B_0 are the initial amounts of A,B, the yield is

$$\frac{A_0}{W} (1 - e^{-k_1 t}) + \frac{B_0}{W} (1 - e^{-k_2 t})$$

and the theoretical ultimate yield is $(A_0 + B_0)/W$. Suppose, however, that k_2 has a much higher activation energy than k_1 such that at low temperatures $k_2 \ll k_1$. Then if the pyrolysis time is limited for practical reasons, the ultimate yield at low temperatures will be A_0/W . At sufficient high temperatures, however, the constant k_2 will be significant and the ultimate yield will reach its theoretical value. Since pyrolysis involves a large number of reaction steps with a wide range of activation energies, the (apparent) ultimate weight loss is an increasing function of temperature. In principle, the ultimate weight loss also depends on the temperature-time history because of the coupled nature of the chemical reactions. However, the dependence on the temperature-time history is rather weak as will be discussed in Chapter 6.

Representative weight loss data from an entrained flow system and a captive sample system are shown in Fig. 4.3 and Figs. 4.4, 4.5 respectively. Figure 4.3 shows the weight loss obtained by the entrained flow technique at high temperatures and short residence times (ref. 57). The data points represent cumulative weight loss corresponding to the pyrolysis time under question. Each point, therefore, corresponds to a distinct experiment employing a different sample of coal particles. The scatter in the data, as high as 20%, is due to measurement error as well as sample variation. Another noteworthy feature is the inflection point at the early stages of pyrolysis, indicating an initial acceleration of the reaction rate. Since the data have been corrected for the effect of heating time, this initial acceleration which has also been observed in other studies seems to be related either to the presence of consecutive reactions or to intraparticle mass transfer retardation.

To prevent secondary reactions of tar vapors on particle surfaces influencing the weight loss, it is necessary to keep very low particle density in the entrained flow reactor. Secondary reactions on the reactor walls would still take place but would only affect the product distribution and not the weight loss.

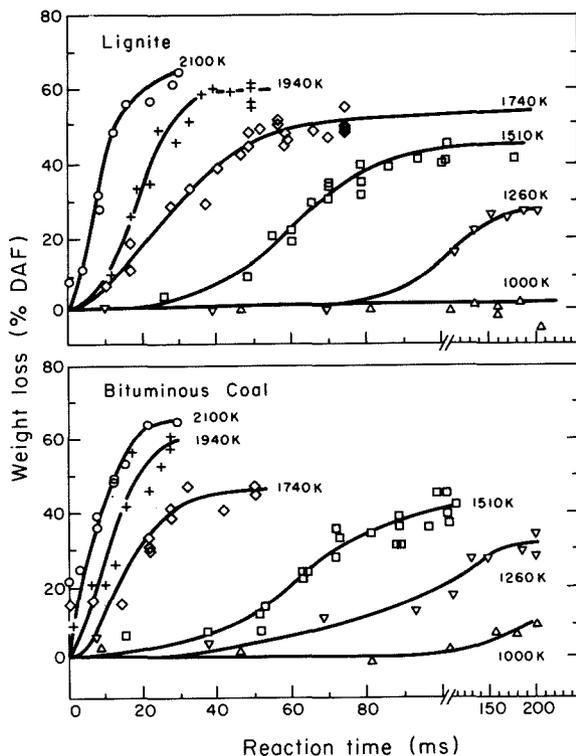


Fig. 4.3. Weight loss vs. pyrolysis time at various furnace temperatures (source: ref. 57).

Solomon and collaborators (refs. 61,70) have studied the pyrolysis of a large number of coals under vacuum (20-60 mm Hg) by the captive sample technique. Figures 4.4,4.5 are representative samples of Solomon's results showing the total weight loss as a function of pyrolysis temperature for two different residence times, 20s and 80s. The weight loss (cumulative) has considerable scatter, some of which may be due to sample variability but a major fraction is probably due to fluctuations in the sample temperature and loss of fine coal fragments from the screen. The solid curves were calculated by a kinetic model discussed in Chapter 6.

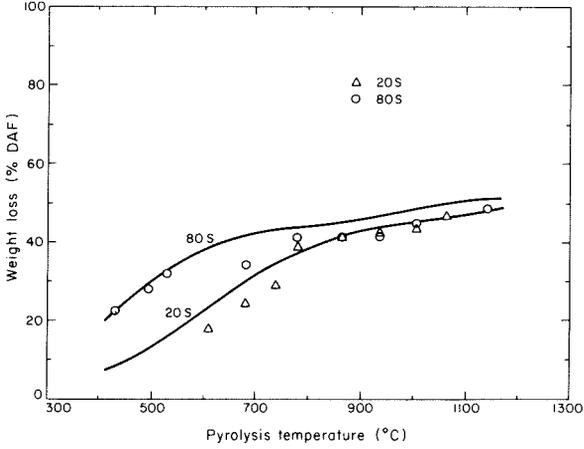


Fig. 4.4. Weight loss vs. temperature for a hvc bituminous coal "Ohio No. 2" (source: ref. 70).

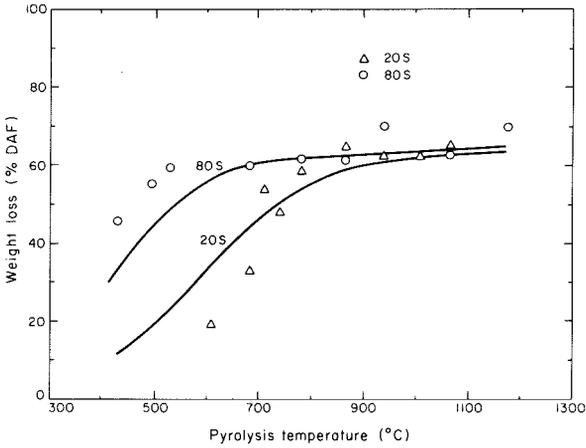


Fig. 4.5. Weight loss vs. temperature for a hva bituminous coal "Lower Kitanning" (source: ref. 70).

The results of Figure 4.4 exhibit some important trends. Above about 700°C the weight loss at 20 and 80s is the same, within experimental error, indicating that 20s is adequate to attain the ultimate asymptotic value. At temperatures below 700°C the deviation between the results at the two residence times is significant indicating that 20s is insufficient for achieving the ultimate weight loss.

Figure 4.5 presents the weight loss for a bituminous coal with the rank "high volatile A". The main difference with Figure 4.5 is in the ultimate weight loss which seems to change very little with temperature above 900°C. This difference will be explained below in the discussion of individual product yields.

4.2.2 Product distribution

The product distribution is the most essential information relative to the commercial utilization of pyrolysis and at the same time sheds considerable light on reaction mechanisms. Representative experimental data are shown in Figs. 4.6-4.8 taken from Solomon's work (ref. 70). They present the cumulative yields of tar, H₂O, CO₂, CO, H₂ and hydrocarbon gases at residence times of twenty seconds. The balance is the residual solid, char. The label T + M denotes tar and "missing" material that escaped the collection procedure and is estimated only by an overall mass balance. This missing material probably consists largely of tar whence lumped with the collected tar. The solid lines again represent results of model fitting. Despite the cumulative nature of the product yields, the scatter in the data is considerable demonstrating the difficulties inherent in such measurements. Measuring the instantaneous (or differential) yields in this experimental setup is clearly impractical.

The products can be classified into two groups relative to the temperature dependence of the yields. Tar, water and carbon dioxide evolve at lower temperatures with ultimate yields that are essentially independent of temperature above 700°C. The second group of products consisting of gaseous hydrocarbons, carbon monoxide and hydrogen evolve at higher temperatures. The ultimate yield of these products continues increasing with temperature up to 1,000°C or higher.

Coal rank is a very important factor in the distribution and temperature dependence of various products. In bituminous coals, tar makes up 50-80% of the weight loss, the remaining consisting of hydrocarbon gases, water and carbon oxides. In subbituminous coals, water and carbon oxides are produced at increased yields, as much as 60% of the weight loss, while tar contributes only 25-40%. In lignites tar is even lower and gases higher as illustrated in Fig. 4.6.

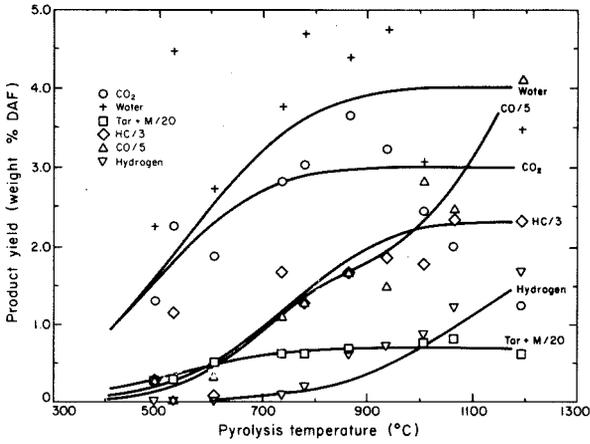


Fig. 4.6. Product yields vs. temperature for a Montana lignite at 20s pyrolysis time (source: ref. 70).

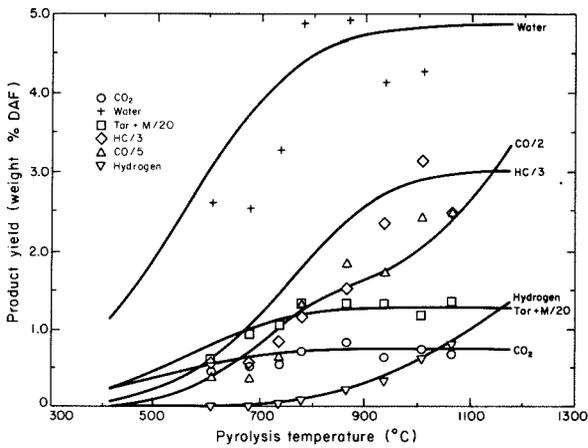


Fig. 4.7. Product yields vs. temperature for a hvc bituminous coal "Ohio No. 2" at 20s pyrolysis time (source: ref. 70).

The variation of the relative distribution of tar and gases among coals of different rank explains the previously observed temperature dependence of the ultimate yield. In bituminous coals where the weight loss is dominated by tar, the ultimate yield appears to increase very little beyond 700°C. In subbituminous coals and lignites, where a considerable fraction of the volatiles consists of CO and hydrocarbon gases, the ultimate weight loss continues increasing with temperature even beyond 1,000°C.

Tar is the most abundant and commercially valuable product from the pyrolysis of bituminous coals. It is a mixture of many compounds with molecular weights mainly in the range 200-1200. At the temperature of pyrolysis it is produced as a vapor but at room temperature it becomes a viscous liquid or solid. The tar liquids consist largely of dimers of smaller fragments generated by the primary bond dissociation reactions.

In an ideal experimental setup, once released from the coal particles the tar molecules are removed from the high temperature region escaping secondary reactions. The captive sample and entrained flow techniques approximate this desirable operation. Figure 4.9 shows the cumulative tar yield at two pyrolysis times, 20s and 80s, as a function of temperature. Despite the large scatter in the data, the ultimate yield (80s) is clearly independent of temperature above 500°C. As a matter of fact, the yield at 80s seems to slightly decline when the temperature exceeds 800°C. This behavior, which has been observed with several other coals, seems to arise from secondary reactions which are more pronounced at higher temperatures and longer reaction times. It is also observed that the 80s yield exceeds the 20s yield up to about 700°C where they become practically indistinguishable. This indicates that at 700°C (perhaps even lower) a pyrolysis time of 20s is sufficient for the attainment of the ultimate yield of tar.

The temperature-time behavior of the yield of hydrocarbon gases, also shown in Fig. 4.9, is considerably different from that of tar. The ultimate yield increases with temperature in the whole range studied. Moreover, the 80s curve considerably exceeds the 20s curve up to about 900°C indicating the generally higher activation energy of the respective rate determining steps.

Another detailed study of individual product yields was conducted by Suuberg et al., also using the captive sample technique (refs. 63,64,71,72). Because the experiments employed nonisothermal temperature pulses, the measurements do not permit the ready visualization of the dependence on time and temperature, although they are amenable to kinetic analysis as will be discussed in the next chapter. Other results concerning product distribution in flash pyrolysis can be found in refs. 65,67,73-75.

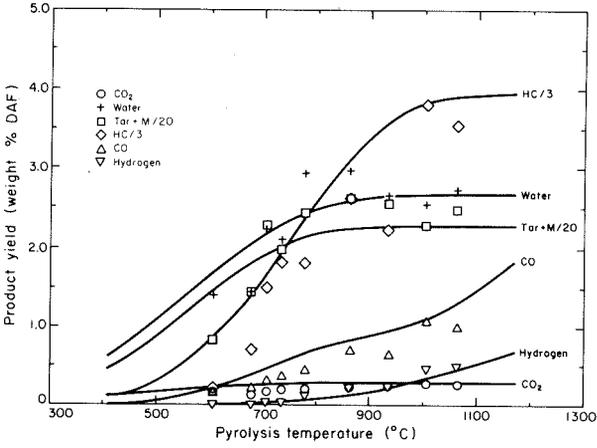


Fig. 4.8. Product yields vs. temperature for a hva bituminous coal "Lower Kittaning" at 20s pyrolysis time (source: ref. 70).

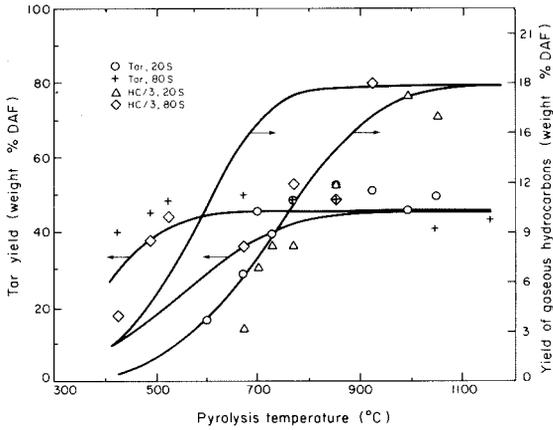


Fig. 4.9. Yields of tar and gaseous hydrocarbons vs. temperature at two pyrolysis times for a hva bituminous coal "Lower Kittaning" (source: ref. 70).

4.2.3. Char and tar composition; distribution of sulfur and nitrogen.

In the previous subsection we presented data on the yields of tar, char and several gaseous compounds. In this subsection we discuss the elemental composition and certain other properties of char and tar with an eye towards their mechanistic significance. We also summarize data about the partition of sulfur and nitrogen among tar, char and gases, which is important to the utilization of these pyrolysis products as fuels.

Figure 4.10 and 4.11 display the elemental composition of char and tar as functions of pyrolysis temperature for a high volatile bituminous coal studied by Solomon (ref. 70). The effect of temperature on hydrogen, oxygen and carbon is quite predictable. Increasing temperature is accompanied by a sharp decrease in the fractions of oxygen and hydrogen due to the evolution of water, carbon oxides and light hydrocarbons, all of which possess O/C or H/C ratios higher than the parent coal. The sulfur content in the char is almost always lower than in the parent coal. However, the temperature dependence of the sulfur varies with the coal examined, probably due to the different amounts of inorganic and organic forms. The nitrogen content in the char is somewhat higher than in the parent coal.

The elemental composition of tar (Fig. 4.11) follows rather different trends. Compared to the parent coal, tar is moderately enriched in hydrogen and sulfur, considerably depleted in oxygen and approximately unchanged in carbon and nitrogen. With increasing temperature, hydrogen decreases slightly, while carbon remains essentially constant. The temperature dependence of oxygen is erratic, perhaps due to the error involved in determination by difference. With some exceptions, the sulfur content is higher than in the parent coal but the temperature dependence is erratic and varies from coal to coal. The content of nitrogen is generally similar to that in the parent coal and shows no noticeable temperature trend.

The distribution of sulfur in the pyrolysis products can be examined in more detail in Fig. 4.12 (ref. 70) which gives organic and total sulfur normalized with respect to the composition in the parent coal. All of the sulfur in the tar is, of course, organic. The normalized organic sulfur is below one in both tar and char, evidently due to the decomposition of reactive sulfur forms like mercaptans and sulfides with the formation of gaseous products, mainly hydrogen sulfide. In some coals with high pyritic content, the organic sulfur content increases with temperature in both the char and tar due to incorporation in the organic structure of decomposing pyritic sulfur. In other coals the organic sulfur shows little temperature trend although it always remains below one. The total sulfur in the char is somewhat less than unity and slightly declines with temperature. References 70 and 76 by Solomon provide detailed results and discussion about the evolution of sulfur forms during pyrolysis.

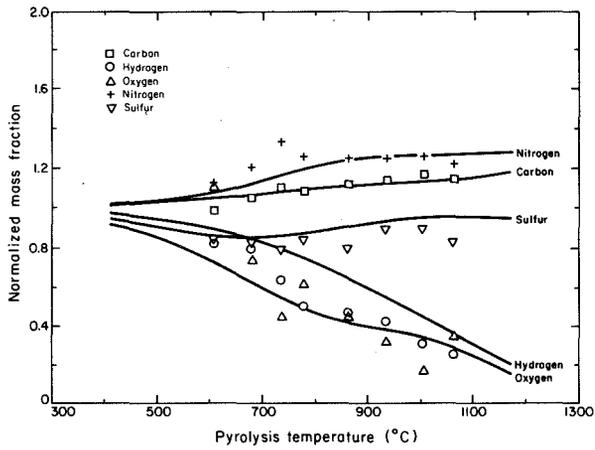


Fig. 4.10. Char composition vs. temperature for a hvc bituminous coal "Ohio No. 2" at 20s pyrolysis time (source: ref. 70).

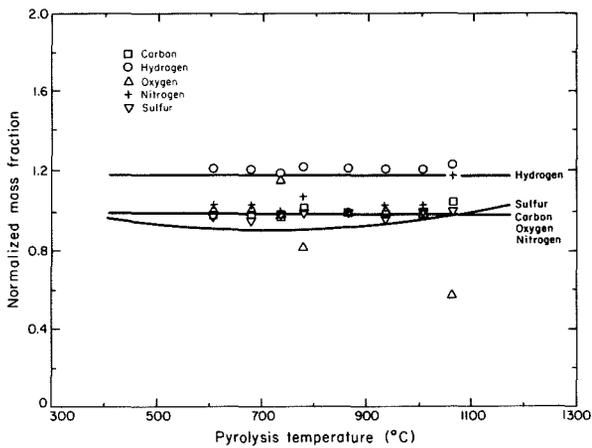


Fig. 4.11. Tar composition vs. temperature for a hvc bituminous coal "Ohio No. 2" at 20s pyrolysis time (source: ref. 70).

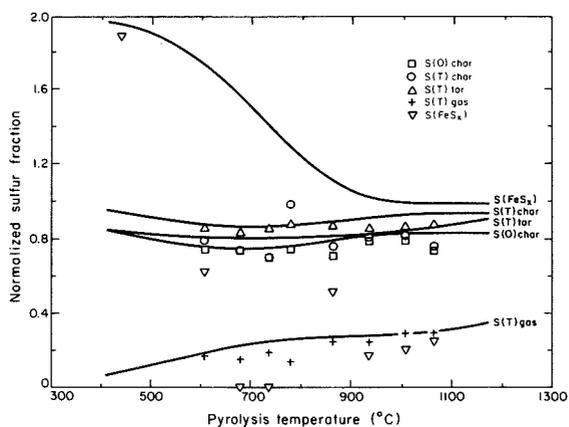


Fig. 4.12. Distribution of sulfur in pyrolysis products of a hvc bituminous coal (Ohio No. 2) vs. temperature at 30s; O: organic, FeS_x: as sulfide of iron, T: total (source: ref. 70).

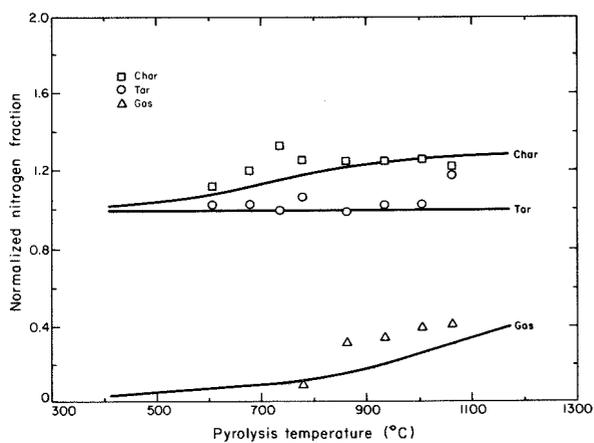


Fig. 4.13. Distribution of nitrogen in pyrolysis products of a hvc bituminous coal (Ohio No. 2) vs. temperature at 30s (source: ref. 70).

Figure 4.13 is an example of the nitrogen distribution in char, tar and gases (ref. 70). The normalized nitrogen in the tar is close to unity indicating that evolving tar molecules contain nitrogen functional groups in the same abundance as in the coal. Char, on the other hand, contains a larger amount of nitrogen while the gases a correspondingly lower amount.

The evolution of nitrogen at higher pyrolysis temperatures typical of pulverized combustion has been studied by Blair et al. (ref. 67) and Pohl and Sarofim (ref. 77). Figure 4.14 shows weight loss and nitrogen loss as a function of temperature, clearly indicating the significant decrease in the nitrogen content of char. Figure 4.15 shows the ultimate weight loss and nitrogen in the char as a function of temperature for coals heated in crucibles. Although these experiments involve slow heating they clearly show the nitrogen content to decline to almost zero as the temperature increases from 1000 to 2000°C.

The interpretation of the results shown in Figs. 14 and 15 is quite straightforward. Below 1000°C nitrogen evolves only with the tar while the gases are almost nitrogen free. As a result the char is gradually enhanced in nitrogen. Above 1000°C various forms of ring nitrogen in the char decompose with the evolution of products such as HCN resulting in a decrease of the nitrogen content.

In addition to the elemental analysis of char and tar, Solomon (ref. 78) and Solomon and Colket (ref. 79) obtained Fourier transform infrared spectra and ^{13}C - ^1H cross polarization nmr spectra. Figures 4.16 and 4.17 are reproduced from this work. An inspection of Figure 4.16 shows the infrared spectra of coal and tar to be remarkably similar indicating similar types and concentrations of bonds. Figure 4.17 shows the nmr spectra of coal, tar and low temperature (<1000°C) char, in each case the broad peak representing aromatic and the narrow peak aliphatic carbon. Coal and tar have identical values for the aromaticity f_a while char a somewhat higher value. The spectrum for the liquid product, tar, has considerably more detail than the spectra for the solid materials.

Further characterization of the chemical structure of tar was carried out by Gavalas and Oka (ref. 7). Three coals characterized in Table 4.1 were subjected to pyrolysis under vacuum at 500°C for 30s. The tar collected was separated by gel permeation chromatography into three molecular weight fractions: L(>1000), M(700-1000) and S(300-700). Each fraction was characterized by ^1H nmr and elemental analysis. The results are shown in Table 4.2 along with corresponding results for tetrahydrofuran extracts of the same coals.

A perusal of Table 4.1 shows coal to be closer in elemental composition to its tar than its extract especially when the CO_2 evolved at 500°C is deducted when computing the elemental composition. Tar has essentially the same carbon content as the coal but somewhat higher hydrogen and slightly lower oxygen contents. The extracts on the other hand have substantially lower oxygen content.

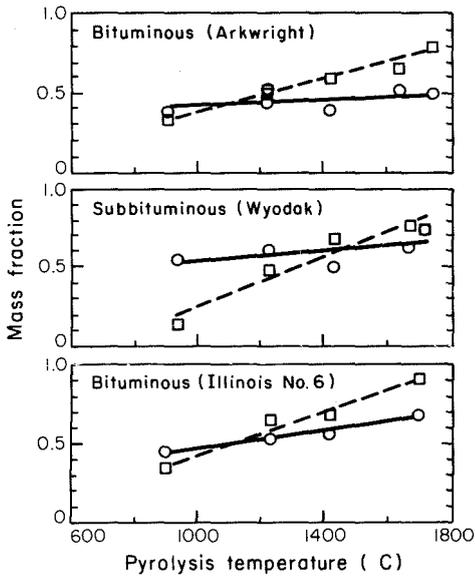


Fig. 4.14. Weight loss (—) and nitrogen loss (----) vs. temperature (source: ref. 67).

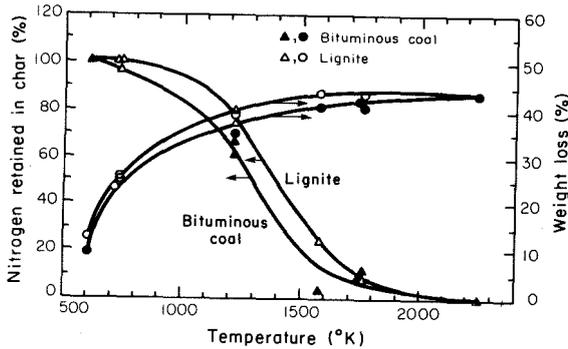


Fig. 4.15. Weight loss and nitrogen retention in char for coal heated in crucibles (source: ref. 77).

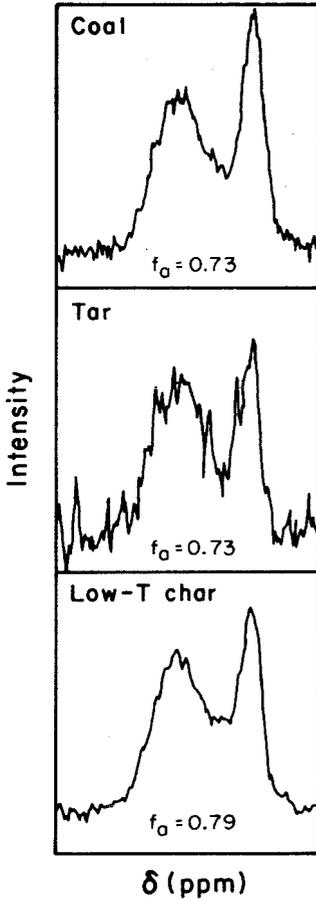


Fig. 4.16. ^{13}C - ^1H cross-polarization spectra of a hva bituminous coal, its tar and low temperature char (source: ref. 79).

The ^1H nmr data of Table 4.1 reveal that more than two-thirds of the hydrogen is in aliphatic form. However, the split between H_α (alpha) and $\text{H}_{\beta+}$ (beta or further from the ring) varies with the rank of the coal. The $\text{H}_{\beta+}$ predominates in the subbituminous coal indicating long chains or hydroaromatic structures while $\text{H}_{\text{ar}+\text{o}}$, H_α and $\text{H}_{\beta+}$ are present in about the same amounts in the two bituminous coals.

The molecular weight data of Table 4.2 show the middle fraction (M) to comprise about half of tar and extract. At the same time, the heavy fraction (H) is more abundant in the extract while the light fraction (L) is more abundant in the tar.

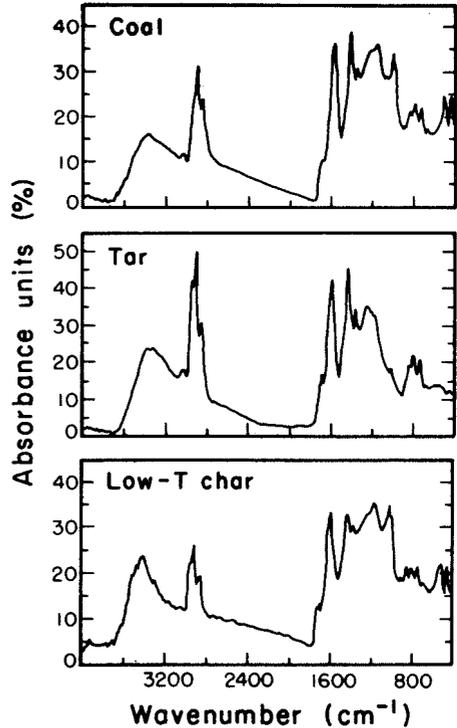


Fig. 4.17. Infrared spectra of a hva bituminous coal, its tar and low temperature char (source: ref. 79).

TABLE 4.1

Elemental composition of coals(daf), extracts and pyrolysis products (source: ref. 7).

		C	H	N	S	O(diff)
Subbituminous C,	c	72.1	5.00	1.28	0.85	20.7
Wyoming Monarch	cc	75.2	5.35	1.36	0.91	17.2
Seam,	e	77.8	8.75	1.28*	0.85*	11.4
PSOC 241	p	74.8	8.0	1.28*	0.85*	15.1
	c	75.7	5.8	1.60	2.89	14.1
HVC Bituminous,	cc	76.2	5.85	1.62	2.93	13.4
Kentucky No.9 Seam	e	82.1	7.4	1.60*	2.89*	6.0
	p	76.1	7.1	1.60*	2.89*	12.3
	c	85.9	5.75	1.48	0.74	6.2
HVB Bituminous,	cc	86.0	5.75	1.49	0.74	6.0
W. Virginia	e	87.5	7.3	1.48*	0.74*	3.1
	p	85.9	7.25	1.48*	0.74*	4.7

c coal, dry-ash-free; cc coal after subtracting CO₂ evolved by pyrolysis at 500°C for 30s; e coal extracts; p coal pyrolysis products.

* Assumed for the purpose of estimating the oxygen content.

TABLE 4.2

Elemental analysis, molecular weights and nmr data for extracts and pyrolysates (source: ref. 7).

		Sub-bituminous		HVC Bituminous		HVB Bituminous		
Extract (wt %) ^a		4.5		8.0		1.6		
Pyrolysis (wt %) ^b		6.0		19.1		10.5		
GPC* (%) ^e	L	32	26	36	20	32	27	
	M	54	48	48	49	44	42	
	S	14	26	16	31	24	31	
¹ H nmr	(%) ^d							
	H _α	20	23	32	34	32	37	
	H _{β+}	68	58	40	33	37	31	
	H _{ar+0}	12	19	28	33	31	32	
¹³ C nmr	(%) ^e							
	C _{ar}	42	-	58	-	-	-	
	C _{al}	58	-	42	-	-	-	
	(%)							
	L	C	76.1	75.6	81.3	75.1	85.7	85.8
		H	8.9	8.1	7.8	7.1	6.9	6.7
	M	C	77.5	73.7	81.5	76.5	87.6	85.9
		H	8.7	8.3	7.1	7.1	7.6	8.0
	S	C	82.6	76.1	85.5	-	89.5	85.9
		H	8.5	7.3	7.4	-	7.2	6.7

^a+0.5; ^b+1.5; ^c+1; ^d+2; ^e+2

* L, M, S: fractions with molecular weights >1000, 700-1000, and 300-700

4.2.4 Effects of pretreatment and atmosphere of pyrolysis

Studies of pretreatment involve exposure to some agent at specified temperature and time, followed by pyrolysis in an inert gas, as usual. By limiting the temperature and residence time, the extent of thermal decomposition reactions during pretreatment can be minimized. Howard (ref. 80) has reviewed several early publications on pretreatment by nitric oxide, steam and oxygen. Pretreatment by nitric oxide at about 300⁰C (ref. 81) led to a modest loss of hydrogen, a modest gain in oxygen and nitrogen and a substantial loss in the proximate volatile matter. The swelling and agglomerating properties of the coal were significantly reduced. Nitrous oxide had similar properties while nitrogen dioxide reacted much faster, even at lower temperatures, and oxidized the coal more extensively.

Pretreatment by steam has not shown any noteworthy effects. Heating a lignite at about 300⁰C in the presence of steam (ref. 80) produced slight decrease of weight loss and slight change of product distribution from the subsequent pyrolysis.

Pretreatment in oxygen has long been studied as a means of reducing the swelling and agglomerating properties of coal and is, in fact, a necessary step in some of the gasification processes currently under development. Howard (ref. 80) has summarized early studies showing that pretreatment by oxygen increases the yield of carbon oxides and water formed in the subsequent pyrolysis while it decreases the yield of tar and reduces or eliminates swelling and agglomeration. The last effect was attributed principally to a change in the surface of the coal which prevented particle agglomeration even when the particle interior passed through a plastic phase. Forney et al. (ref. 82) found that treatment with a gas containing 0.2% oxygen at 400-425⁰C for five minutes drastically reduced swelling and eliminated agglomeration of a caking coal. Under these conditions, substantial devolatilization could not be avoided. McCarthy (ref. 83) found that pretreatment in an atmosphere of 2-10% oxygen at 400⁰C for a few seconds similarly greatly reduced agglomeration of a caking bituminous coal.

A comprehensive study of the effect of preoxidation on subsequent pyrolysis and the properties of the resulting char was conducted by Mahajan et al. (ref. 84). A strongly caking coal was heated in air at 120-250⁰C for a few minutes to four hours. The weight gain during this treatment increased with temperature and time, not exceeding 6.5% under the most drastic conditions. Figure 4.18 shows the weight loss of coal at different levels of preoxidation as a function of pyrolysis temperature. The level of preoxidation was in all cases fully characterized by the percentage weight gain without reference to temperature and duration of the oxidative pretreatment. Below 450⁰C the level of preoxidation has

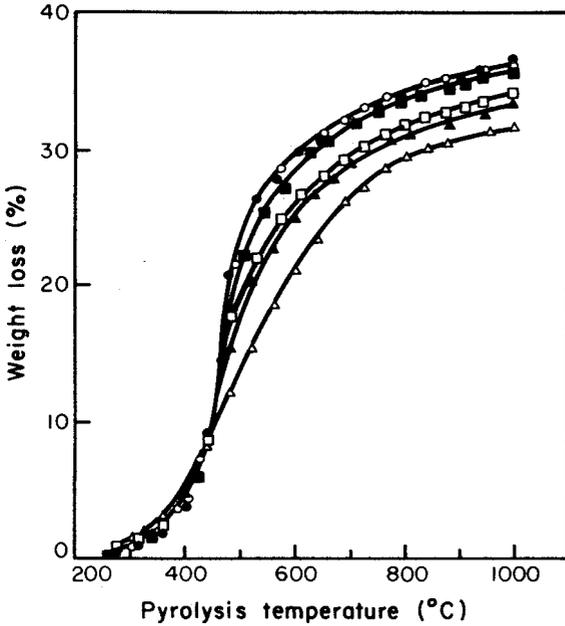


Fig. 4.18. Pyrolysis weight loss vs. preoxidation level for a caking bituminous coal PSOC 337; weight gain during preoxidation (%) ● none, ○ 0.45, ■ 0.75, □ 1.4, ▲ 2.4, △ 7.0 (source: ref. 84).

little effect on the weight loss of pyrolysis but above 450°C the weight loss decreases with the preoxidation level. The results shown in Fig. 4.13 are by no means representative of all caking coals. Working with another caking coal, the authors found a more complex dependence of the pyrolysis weight loss on the level of preoxidation. At pyrolysis temperatures less than 500°C, the weight loss increased with the level of preoxidation but above 500°C the variation became erratic. The complex dependence of weight loss was attributed to the following competing factors. Addition of oxygen produces functional groups, such as carboxyl, which during pyrolysis evolve carbon oxides and water making a positive contribution to the weight loss. At the same time, the production of carboxyl and other oxygenated groups reduces the amount of hydrogen that would otherwise be available for tar generation. To this explanation, one must add that increased water evolution during pyrolysis increases the degree of crosslinking leading again to lower tar yield. In addition to the changes in the weight loss, the chars of preoxidized coals had more open structure, sharply higher CO₂ surface area, and moderately higher reactivity in oxygen.

The pyrolysis experiments discussed until now were all obtained either under vacuum or under an inert gas such as nitrogen or helium. Pyrolysis in a hydrogen atmosphere - hydrolysis - is important in its own right and will be examined separately in chapter 7. Pyrolysis in an oxygen atmosphere is an important

part of combustion. It is generally believed that oxygen does not affect the primary devolatilization reactions, although it rapidly oxidizes the volatiles in the surrounding gas provided the temperature is sufficiently high as in a combustion furnace. Only subsequent to the rapid volatile release, is oxygen able to reach and oxidize the char particles. The effect of oxygen at lower particle temperatures or when the surrounding gas is cold has not been studied as such.

Pyrolysis in H_2O and CO_2 is of some interest but has received very little attention. Jones et al. (ref. 85) compared the fluidized pyrolysis of a wet (20% moisture) or predried subbituminous coal in nitrogen or steam with the results shown in Table 4.3. The term "liquor" in the table indicates the aqueous phase containing the chemical water of pyrolysis along with small amounts of phenolic compounds.

TABLE 4.3

Effect of moisture and fluidizing gas on product yields from the pyrolysis of a subbituminous coal at $1400^{\circ}F$ in a fluidized bed (ref. 85).

	As received		Dried at $300^{\circ}F$	
	N_2	H_2O	N_2	H_2O
Feed moisture %	20	20	0	0
Fluidized gas	N_2	H_2O	N_2	H_2O
Yields (% dry basis)				
Char	54.6	53.0	56.0	53.1
Tar	11.8	11.0	0.0	9.7
Liquor	7.0	8.7	9.6	11.4
Gas	26.6	27.3	25.4	25.8

The results of Table 4.3 indicate that the tar yield is slightly higher from the moist (as received) coal irrespective of the fluidizing gas. The total weight loss is slightly higher for the moist coal or when steam was the fluidizing gas. Although the differences are small and subject to some scatter, one might venture the following conclusion. Drying coal induces changes in the pore structure or the chemical structure that reduce tar and gas production in subsequent pyrolysis. The observed increase in the yield of liquid (chemical water) when steam is the fluidizing gas is rather puzzling and might be due to errors in the material balances. The nature of the fluidizing gas seems to have little effect on the yields of tar and gases suggesting little effect on secondary tar-cracking reactions. Further discussion on the possible effects of H_2O or CO_2 on secondary reactions will be given in a subsequent subsection dealing with the pyrolysis process of the Occidental Research Corporation.

4.2.5 Effect of inorganic constituents or additives on pyrolysis product yields

Broadly speaking, inorganic matter can operate in two forms to influence the pyrolytic or other reactions of coal. One is as discrete inclusions or continuously distributed material within the coal particles. This form consists of the inherent mineral matter of coal or of material added by impregnation or ion exchange. The second form consists of mechanically mixed inorganic material remaining external to the coal particles. The effects of these two forms of inorganic matter will now be examined separately.

The main groups of minerals in coal include clays (e.g. kaolinite and illite), silica (quartz), sulfides (mainly pyrite), carbonates (e.g. CaCO_3), smaller amounts of sulfates and oxides and minor amounts of other minerals. Detailed composition normally refers to the ash, i.e. the inorganic matter remaining after complete oxidation. The transformation of mineral matter to ash involves loss of water from the clays, CO_2 from the carbonates, oxidation of pyrite to iron oxide and fixation of oxides of sulfur in the form of sulfates by calcium and magnesium oxides. The total amount of ash varies widely with coal but generally remains below 25% by weight. The ash composition also varies widely. For example, the composition of the major ash components in American bituminous coals was found in the range SiO_2 :20-60%, Al_2O_3 :10-35%, Fe_2O_3 :5-35%, CaO :1-20%, MgO :0.3-4%, TiO_2 :0.5-2.5%, $\text{Na}_2\text{O} + \text{K}_2\text{O}$:1-4% and SO_3 :0.1-12% (ref. 86). Subbituminous coals and lignites contain larger amounts of CaO and MgO .

An important consideration relative to the catalytic activity of inherent mineral matter in pyrolysis or gasification is size distribution. Mineral matter is generally present in two forms, either as discrete particles of about one micron size or larger, or distributed on a much finer scale, in association with the organic matter. For example, calcium and magnesium in low rank coals are largely present as cations associated with carboxylic groups. Mahajan (ref. 87) refers to measurements of N_2 surface areas as high as 10^2 m²/g for coal minerals corresponding to a mean diameter of about 0.15 μm .

Detailed investigations of the effect of alkaline earth cations on the pyrolysis products of low rank coals have been carried out by Schafer (refs. 88-90). These studies compared acid-demineralized coals with coals that subsequent to demineralization were converted to cation form (Na, K, Mg, Ca, Ba). The measurements included the yields of CO_2 , CO and H_2O at different pyrolysis temperatures. In addition, the carboxylic and phenolic content of the coal before and after pyrolysis was determined by titration. The presence of cations was found to alter the relative yields of the three product gases but not to affect the overall weight loss. For example, the ratio $\text{H}_2\text{O}/\text{CO}_2$ was always smaller for the cation forms compared to the acid form. Significant differences in the gas yields were observed between various cation forms, some possibly due to formation

of cyanide compounds by reactions of the cation with the carrier nitrogen. Comparisons between the CO_2 , CO evolved and acidic content of the coal led to the conclusion that CO_2 derives from carboxyl groups and CO derives from phenolic groups. Water was presumed to derive from some unidentified oxygen group associated with carboxylic groups. These conclusions are at some variance with the work of Brooks et al. (ref. 46) discussed in section 3.7. In a subsequent investigation of the flash pyrolysis of various low rank coals Tyler and Schafer (ref. 91) found that the presence of cations had profound effect on the yields of tar, C_1 - C_3 hydrocarbons and total volatile matter. Removal of cations present in the coals by acid wash increased the yield of tar by as much as a factor of two but had small effect on the yield of hydrocarbon gases. Conversely, addition of calcium ions to the acid-form led to decreased tar and total volatile matter. The fact that the change of the tar yield is not accompanied by a corresponding change of the yield of gases suggests that the effect of cations is not manifested via secondary tar-cracking reactions. Instead it was suggested that the cations might suppress tar evolution either by restricting the micropore structure, or by catalyzing the recombination of metaplast molecules before volatilization could take place.

Mahajan and Walker (ref. 92) studied the effect of demineralization by acid treatment on the N_2 and CO_2 surface areas of a number of coals and their carbonization chars. Very divergent trends were observed among the various coals with the surface areas in some cases increasing, in others decreasing and with N_2 and CO_2 areas not necessarily changing in the same direction. Changes in the porous structure can certainly affect tar evolution but the evidence to date is clearly insufficient for firm conclusions. The alternative explanation based on the chemical role of mineral components is certainly plausible, especially considering that the acid treatment of coal to remove cations could also remove or modify the acidity of clay minerals. Such clays might play some role in tar-forming reactions via carbonium ion mechanisms. Further work to delineate the pyrolytic behavior of cation exchanged coals is desirable especially in view of the potential use of cations as catalysts or sulfur scavengers for gasification and combustion.

The effect of inorganic additives in the form of powders mechanically mixed with coal has also been examined. Yeboah et al. (ref. 93) studied the product yields from a bituminous coal and a lignite pyrolyzed in a fluidized bed in the presence of calcined dolomite particles. The presence of the dolomite resulted in decreased tar yield and increased gas yield in all cases. These changes are clearly due to secondary tar cracking reactions on the surface of the dolomite particles.

A different mode of introduction of inorganic additives was investigated by

Franklin et al. (ref. 94). A Pittsburgh No. 8 bituminous coal was demineralized by extraction with a HF-HCl solution and co-slurried in water for for 24 hours with extremely fine particles (0.1 μm) of calcium carbonate or calcium oxide and calcium carbonate. This pretreatment led to the incorporation of about 20% calcium carbonate. While the form of the added material was not determined, it probably consisted of particles coating the surface or penetrating the larger pores of the coal with smaller amounts incorporated on a finer scale by association with the acidic functional groups of coal. The demineralized coal and the calcium-treated coal were subjected to rapid pyrolysis by the captive sample procedure with the following results. Addition of calcium resulted in substantially lower tar yield (20% versus 30%) and lower yield of light hydrocarbon gases, especially at temperatures above 1100⁰K. At the same time, calcium treated coals gave considerably higher yields of carbon monoxide, carbon dioxide and water. The overall weight loss in the calcium treated coal was decreased at temperatures above 900⁰K. The decreased yield of tar was attributed to secondary reactions of cracking and repolymerization catalyzed by the calcium additive. Such reactions would normally increase the yield of light hydrocarbons. That the yield of these hydrocarbons actually decreased, could be explained by the calcium additive catalyzing the further cracking of methane, ethane, etc. to carbon and hydrogen. Much of the increase in the yield of carbon dioxide was shown to result from the decomposition of calcium carbonate to calcium oxide, a reaction catalyzed by the carbon surface. On the other hand, the increased yield of carbon monoxide was attributed to the decomposition of phenolic groups in the coal structure.

4.2.6 Miscellaneous techniques and results

In this subsection we review some additional pyrolysis studies which did not fit properly in the previous sections. A number of early studies employed thermogravimetric analysis with very low heating rates, a few degrees per minute. The other group of studies employed heating by light, laser light, or plasma arc achieving very high heating rates.

A thermal balance is an apparatus providing continuous measurement of the weight of a static sample under the flow of a carrier gas and linearly rising temperature. Waters (ref. 95) described some early thermal balances and discussed weight loss curves from coal pyrolysis. van Krevelen et al. (ref. 96) used a thermal balance of the torsion type to correlate weight loss with plastic properties. Figure 4.19 shows some typical weight loss curves obtained with a low volatile bituminous coal. The chief features of these curves are (i) The S-shape of the cumulative weight loss. The initial acceleration of the curve, observed also in section 4.2.1, could be due to consecutive reactions or the solubility of some pyrolysis products in the coal melt. (ii) The temperature

of maximum devolatilization rate increases with increasing heating rate. More recently, Ciuryla et al. (ref. 97) employed a modern thermobalance to study the weight loss of coals of different ranks under heating rates 40-160⁰/min. As in earlier studies, maximum rate of devolatilization increased with heating rate. The cumulative yield at a final temperature of 1000⁰C was found independent of the heating rate, in agreement with the studies reviewed in the previous subsections. The weight loss data were fitted successfully by the Pitt-Anthony model of distributed activation energies.

The principal advantage of the thermogravimetric technique is the continuous and accurate weight measurement. Its chief disadvantages is the inability to operate at high heating rates and constant temperatures and the difficulty to measure accurately the sample temperature. Isothermal operation must always be

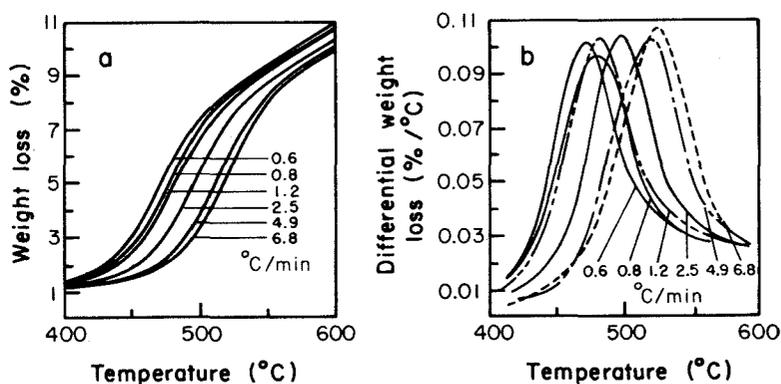


Fig. 4.19. Thermogravimetric analysis of a low volatile bituminous coal. Cumulative (a) and differential (b) weight loss vs. temperature at different heating rates (source: ref. 96).

preceded by a period of slow linear heating. With current commercial models, the sample size can be varied from a few milligrams to about a gram. With large sample size, the sample temperature is uncertain and secondary reactions may become important. Using a small sample size and a sweep gas minimizes secondary reactions but renders product analysis difficult. In fact, none of the aforementioned studies measured individual product yields. Combination of continuous and accurate weight measurement with continuous analysis of gaseous products by infrared and flame ionization detectors seems a most promising technique despite the restriction to low heating rates.

The kinetic feature of constant and slow heating rates has been employed without the gravimetric capability, simply by placing the coal sample in a furnace under the flow of a sweep gas. Using a suitably large sample, of the

order of one gram, it is relatively straightforward to measure the instantaneous rate of generation of individual gaseous species at the cost, of course, of allowing secondary reactions on the particle surface. Experiments of this type have been carried out by Fitzgerald and van Krevelen (ref. 98) and Juntgen and van Heek (ref. 66).

Investigation of pyrolysis in the context of pulverized combustion requires very high heating rates in the range of 20,000 - 100,000 °C/s. One experimental technique for achieving such rates in a small scale apparatus is the irradiation of coal with ordinary or laser light. Sharkey et al. (ref. 99) irradiated coal in the form of 3/8" cubes or a fine powder with light from a xenon lamp or a ruby laser operating at specified power levels. The coal temperature attained under these conditions could not be determined but was estimated to be in excess of 1000°C. The product yields obtained under irradiation compared to those obtained under ordinary carbonization showed much higher contents of acetylene (absent in carbonization) and carbon oxides and sharply lower content of methane. These results were attributed to the higher temperatures prevalent under irradiation. However, the yields of hydrocarbons other than methane and acetylene exhibited irregular and on the whole obscure variations. Evidently, secondary reactions in the gas phase, as well as in the solid phase, are responsible for the overall product distribution.

Granger and Ladner (ref. 100) analyzed the gaseous products of several coals under irradiation from a xenon lamp with and without a filter to remove the UV component of the light. Their small scale apparatus allowed variation of the incident energy and their analysis included gaseous products, i.e. carbon oxides and light hydrocarbons. Water was not determined and tar was estimated rather crudely. Figure 4.20 shows the major pyrolysis products versus total incident energy. The principal feature of the results is the rapid increase in hydrogen, acetylene and carbon monoxide with increasing light intensity. The rapid increase in carbon monoxide is easily accounted by the fact that this gas is the only oxygen-containing product after the evolution of carbon dioxide has been completed in the initial phases of pyrolysis. The latter gas was actually absent, evidently being converted to carbon dioxide and carbon at the high temperatures of the experiment. The yield of tar was found to pass through a maximum as a result of secondary cracking reactions. The results of Fig. 4.20 were obtained using UV-filtered radiation. Unfiltered light resulted in decreased yields of olefins and paraffins and increased yields of carbon monoxide, hydrogen, acetylene and soot. These changes indicate the presence of photochemical cracking reactions in the gas phase.

A technique for heating coals at very high temperatures and heating rates is the plasma arc. Bond et al. (ref. 101) used an argon plasma jet to pyrolyse

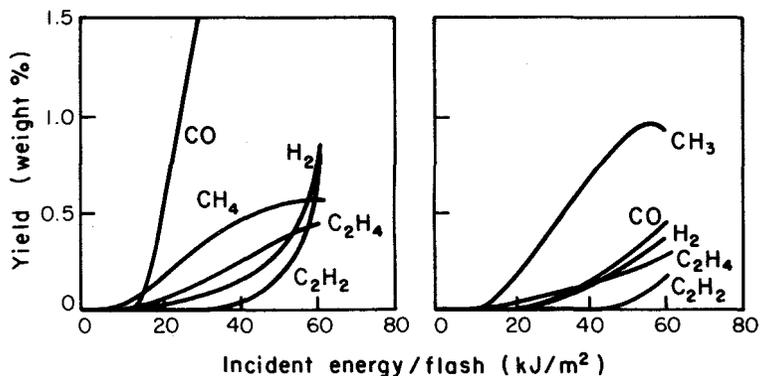


Fig. 4.20. Yields of gaseous products from the flash pyrolysis by xenon light of a noncaking (a) and a caking (b) coal (source: ref. 100).

coals of various ranks. The device provided rapid heating and quenching of the pulverized coal particles. Temperatures at the center of the jet were estimated to be between 10,000 to 15,000^oC. The maximum temperature attained by the coal particles could not be determined but was estimated to be well in excess of 1000^oC. The products were gas and soot with tar completely absent. The gas contained mainly hydrogen, carbon monoxide and acetylene, which comprised over 95% of all hydrocarbon gases. Acetylene yields as high as 20% by weight of the coal were obtained. Overall conversion increased with decreasing particle size and with increasing proximate volatile matter of the starting coal.

A thermodynamic analysis of product distribution from ultrahigh temperature coal pyrolysis in various atmospheres was made by Griffiths and Standing (ref. 102). Although, in each case the equilibrium mixture contains free radicals as well as stable species, attention can be limited to stable species assuming suitable radical recombination during quenching. At temperatures above 1800^oK, acetylene is the most stable among hydrocarbons, although unstable with respect to carbon and hydrogen. Above 3,000^oK, the yield of acetylene at equilibrium with carbon and hydrogen becomes significant. The oxygen present in coal probably ends up as carbon monoxide, however, oxygen was not considered. In the presence of nitrogen, the equilibrium yields of cyanogen and hydrogen cyanide are also significant. The actual product yields obtained in a practical configuration such as a plasma arc probably do not reach thermodynamic equilibrium because of insufficient residence times.

4.3 PYROLYSIS PROCESSES

Pyrolysis is the simplest means of upgrading coal to higher quality fuels. Merely by heating, coal decomposes to gases, tar liquids and char. The gases can be readily burned in an industrial furnace. The tar is the most valuable product because it can be hydrotreated to clean liquid fuels. The char must be utilized in an industrial or utility furnace or gasified to a low Btu or synthesis gas. Because of its low content of volatiles char has poor ignition characteristics and may require special burners or some other means of maintaining flame stability. It can always be burned in a fluidized furnace.

The simplicity of the basic flow sheet of pyrolysis as a coal conversion process obscures a number of mechanical difficulties that have slowed down its commercial development. Chief among these difficulties is the caking and agglomerating properties of high volatile bituminous coals upon heating. Those very coals are also the most interesting for their high yield of tar liquids. Rapid heating of coal in a configuration that limits the extent of secondary reactions is another difficulty that has not been entirely overcome. Finally, collecting tar liquids and removing suspended fine solids is also a problem, common to other coal conversion processes. The two processes discussed below have at least partially overcome the mechanical problems associated with rapid heating and agglomeration.

4.3.1 The COED process (refs. 103-105)

The COED process (Char-Oil-Energy-Development) was developed by FMC corporation under contract from the office of coal research (subsequently absorbed into ERDA which in turn was absorbed into the department of energy). The development effort reached the stage of a 36 ton-per-day pilot plant tested in the period 1971-1973. Since then, research and development activities were redirected to a related gasification process (COGAS) under private sponsorship.

The central part of the process is shown in the schematic diagram of Fig. 4.21. Coarsely ground coal (<1 mm diameter) is dried and fed to fluidized bed I operating at 600°F with hot combustion gases. The volatiles from I flow to the product recovery system while the char is carried to fluidized bed II operating at 850°F and subsequently to fluidized bed III operating at 1000°F. Char from stage III is carried to fluidized bed IV (1600°F) where it is partially burned with oxygen. Hot char from stage IV is recycled to stage III to provide part of the required heating. The effluent gases from stage IV provide additional heating as well as fluidizing for stage III. The hot product gases from stage III in turn provide the heating and fluidizing medium for stage II. The gaseous and liquid products from stages I and II are separated. Part of the gases is burned to provide the fluidized medium for stage I, the remainder collected as an end product of the

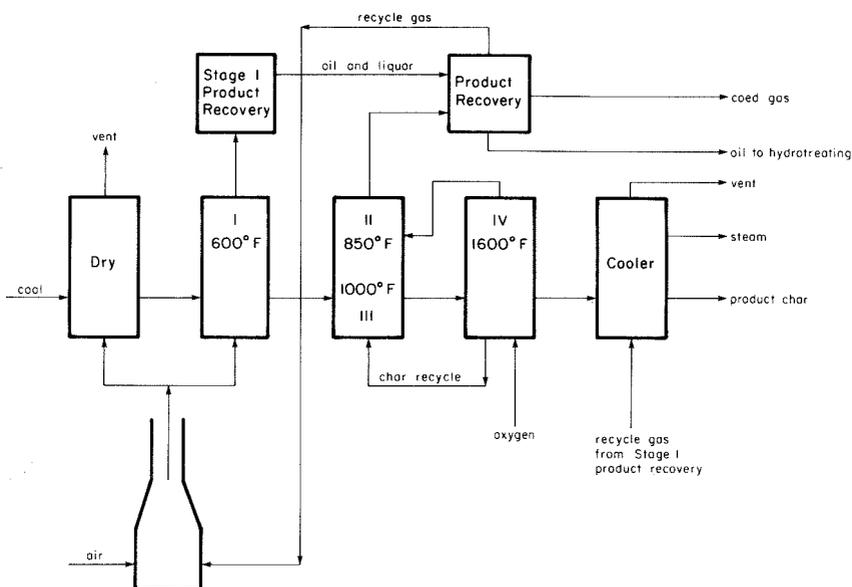


Fig. 4.21. The COED process flowsheet (source: ref. 103).

process. The product liquids are hydrotreated to clean liquid fuels for stationary or portable powerplants.

Carrying out the pyrolysis in four coupled fluidized beds provides the required heating and at the same time prevents caking and agglomeration. As coal (or char) progresses through stages I-IV its caking temperature increases due to the successive loss of volatiles. Thus maintaining the temperature of each stage lower than the caking temperature of the fluidized char prevents its softening and agglomeration. On the other hand, the prolonged contact of volatiles with the fluidized char result in extensive secondary reactions. Another adverse factor in terms of secondary reactions is the relatively large particle size. Compared to the tars produced in the laboratory reactors described in section 4.1, the COED liquids are produced at lower yields and have lower boiling points and less polar character, whence the term "oils".

A ton of high volatile bituminous coal treated by the COED process yields about 1.4 barrels of oil or about 18% by weight, well below the 30-50% laboratory yields by the captive sample technique. The other products from one ton of coal are char, about the same as the ASTM proximate analysis, and 8000-9000 scf of gases of heating value about 540/scf. The relatively low yield of liquid products

is probably the main reason why the COED process has been dropped from the small list of liquefaction processes scheduled for commercialization.

4.3.2 The Occidental Research Corporation (ORC) process (ref. 106)

The ORC process has been under development since 1969. The original experimental work at the laboratory scale was internally funded. Subsequent work utilized the laboratory unit and a three ton-per-day process development unit which was tested in the period 1976-1978 under contract to the department of energy.

A schematic of the ORC process flowsheet is shown in Fig. 4.22. Coal is pulverized (median size 20-40 μm), dried and pneumatically transported to the pyrolysis reactor where it is mixed with hot recycle char. Solids and gases move co-currently downward through the reactor and are collected in a cyclone. The solid stream from the cyclone is split in two parts. One part is carried to an entrained flow vessel for partial burning and recycling to the reactor. The remainder is removed as the product char. The volatiles from the cyclone are rapidly quenched and separated into a fuel gas and a liquid product which after hydrotreating provides the main process product.

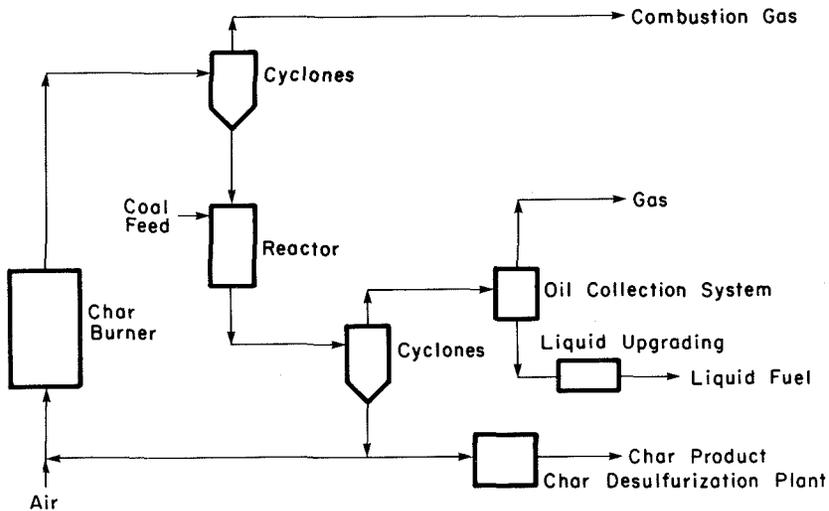


Fig. 4.22. Schematic of the ORC pyrolysis process (source: ref. 106).

Some of the key operating parameters in the reactor are temperature (1000-1400°F), pressure (5 psig) and ratio of recycled char to coal, about 10:1. The results from the bench scale reactor (BSR) and the pilot plant or "process development unit" show some important differences and will be discussed separately.

The bench scale unit consisted of an externally heated entrained flow reactor. Recycle char was not used in this system since the main objective was to determine the dependence of product yields on temperature and residence time. Figure 4.23 shows the yields of the major pyrolysis products as functions of temperature for two residence times, 1.5s and 3.0s. The most interesting feature of the figure is the maximum in the tar yield at about 1200°F. The maximum yield of about 20% is twice the amount obtained in the standard Fischer assay. As the temperature increases beyond 1200°F the tar yield declines, evidently due to secondary reactions occurring homogeneously or on the reactor walls.

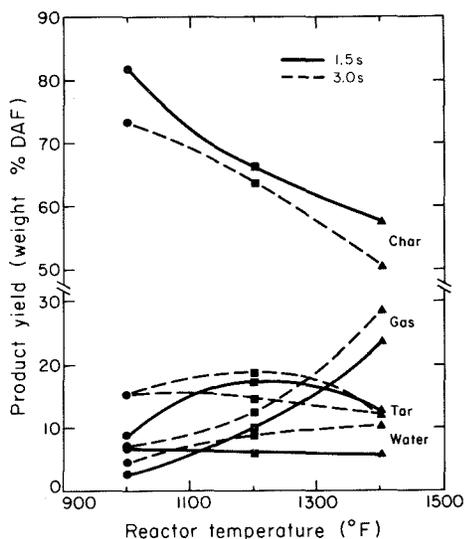


Fig. 4.23. Product yields vs. temperature from the pyrolysis of a subbituminous coal in the BSR (source: ref. 106).

Pyrolyzing the subbituminous coal in the process development unit under similar operating conditions but with hot char recycle gave a surprisingly different product distribution. The tar yield was limited to only about 7-10%, while char and gases were produced in increased quantities. Since the only essential difference between the operation with the BSR and PDU was the presence of the recycle char, the difference in the tar yields was attributed to adsorption and cracking on the char surface. To confirm this explanation additional experiments were performed with increased amounts of recycle char. Changing the char to coal ratio from 10:1 to 40:1 was found to decrease the tar yield from 10% to 4%.

Continuing efforts to improve the tar yield resulted in an unexpected finding. When the inert N_2 carrier was replaced by CO_2 or H_2O , the maximum tar yield from the PDU operation increased to 18-22%, a level identical to that obtained with the BSR. This important and surprising result was attributed to the adsorption of CO_2 and H_2O on the active sites of the char's surface which would otherwise catalyze the cracking of tar molecules. In other words, CO_2 and H_2O compete with tar for the same active sites on the char's surface.

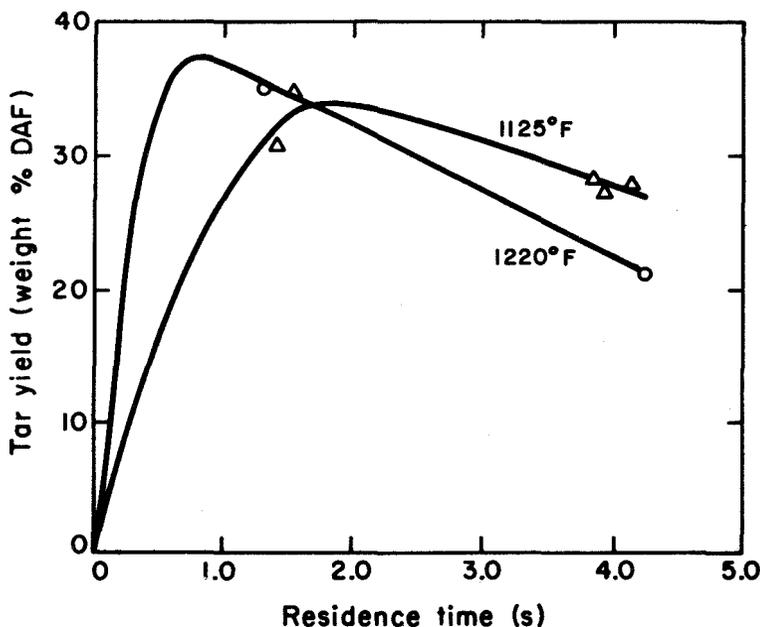


Fig. 4.24. Tar yield vs. residence time from the pyrolysis of a bituminous coal in the PDU (source: ref. 106).

The results discussed up to this point concern the pyrolysis of a subbituminous coal. PDU experiments were also performed with a high volatile bituminous coal (hvc, Kentucky No. 9). Figure 4.24 shows the yield of tar as a function of temperature at two residence times. The maximum yield of about 38% would be quite attractive on a commercial scale. The decline of the yield with increasing residence time is again due to secondary reactions. Surprisingly, the tar yield for the bituminous coal was found to be essentially independent of the carrier gas (N_2, CO_2, H_2O). The strikingly different behavior of the two coals has not been explained and certainly deserves systematic study.

At this point we return to an earlier observation that the caking and agglomerating properties of coal constitute the chief technical difficulty in the commercialization of pyrolysis. The ORC process has approached the difficult problems of coal agglomeration by a special design of the top part of the PDU reactor where the mixing of coal and recycle char takes place (see Fig. 4.25). Pulverized coal is injected by a jet of carrier gas in a surrounding stream of hot recycle char descending downwards from a shallow fluidized region. It is vital that the coal particles are heated rapidly to complete their caking phase before reaching the reactor walls. Small particle size and large char to coal ratio are necessary for this purpose.

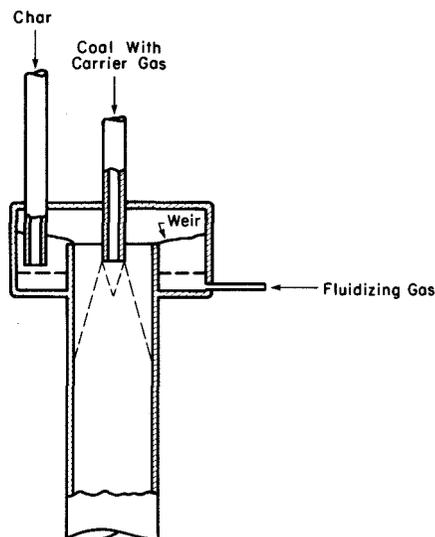


Fig. 4.25. Device for injecting and mixing of coal and char in the PDU (source: 106).

The reactor design shown in Fig. 4.25 was only partially successful. During operation with the bituminous coal the PDU encountered flow instabilities limiting continuous operation to less than one day. A momentary decrease in the char flow rate would cause the deposition of plastic coal particles on the injector tip or the reactor walls. The resulting decrease in the cross section would in turn further reduce the char flow rate and so on, leading eventually to a complete flow stoppage. Although improved designs evolved during the testing, a completely satisfactory operation was not achieved.

Assuming that the mechanical difficulties will eventually be resolved, the ORC process appears a most promising route to coal liquids by virtue of its simple flowsheet and the high yield of tar.